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A critical review of sampling standards for solid biofuels – Missing contributions from the Theory of Sampling (TOS)

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ABSTRACT

Current standards for biofuel dealing with sample extraction, mass reduction and sample preparation are assessed with respect to the principles for representative sampling as set forward in the Theory of Sampling (TOS), which constitutes the only complete, scientific theory for sampling. Practical industrial sampling constitutes the only source for gaining data for reliable process monitoring and control – but involves a high error potential if not based on unambiguous, representative samples. For the comparatively new sector of biomass combustion or co-firing of biomass in converted coal power plants, reliable quality measures are crucial to assure stable fuel quality and for being able to optimize the combustion process. All so-called “incorrect sampling errors” (incorrect delineation, – extraction and – preparation) must be identified, reduced, if not altogether eliminated, lest representativeness is impossible. For reaching this target and to ensure representative sampling, a minimum working understanding of TOS is required. Sampling standards serve the purpose to delineate the foundation and assurance for reliable, representative sampling under all circumstances for the material class(es) involved, and must for this reason be in full compliance with TOS. This critical review shows that many recommended or allowed sampling procedures for solid biofuels do not comply herewith, and neither are all the necessary rules of TOS followed for the subsequent mass reduction procedures in the analytical laboratory. We point out all such error sources in the current standards and discuss what measures are necessary to rectify this incomplete state-of-affairs. The current review is but one activity within the context of formulating an even more general, “horizontal” sampling standard intended to cover all material classes.

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1. Introduction

The global climate is in clear and present danger, expected to undergo major and irreversible changes in the very near future, unless emissions of greenhouse gases (GHGs) are reduced significantly, in particular CO_2 from combustion of fossil fuels. In the reference scenario of the International Energy Agency (IEA) global emissions of GHGs are expected to increase from 42.4 Gt CO_2 equivalent in 2005 to 68.4 Gt in 2050 [1]. As a reaction to the current climate changes, the EU has defined a very ambitious long-term objective to reduce GHG emissions by 80–95% by 2050 for developed countries as a group, which has been adopted by the European Council in 2009.

An effective contribution to become fossil fuel independent and to lower significantly CO_2 emissions is the conversion of coal-fired power plants to biofuel or co-fired based combustion. The Danish state is a good example for this transition. The Danish Energy Agency states that by 2020 Denmark should be among the three most energy-efficient countries in the OECD and that in a long-term perspective Denmark should become independent of fossil fuels such as coal, oil and gas in order to reach its objective to reduce national CO_2 emissions by 21% as stated in the Kyoto target.

In 2008 Denmark's CO_2 emissions from coal combustion amounted to approx. 16 Mt CO_2 equalling more than 30% of the total fuel related emissions of 48 Mt CO_2 [2]. Since biofuels absorb the same amount of CO_2 during growth, which is later released during combustion, the CO_2 emitted from coal-fired power plants can be lowered significantly when converted to biofuel-based power plants. The goal here is "carbon-neutral" energy production. However, when considering the entire life cycle of biofuels as combustion fuels, a certain amount of CO_2 is also emitted due to treatment and transportation of the biofuels. Nevertheless the total amount of emissions is very significantly lower when compared to coal as a combustion fuel.

The terminology, definitions and descriptions of solid biofuels have been standardized in [3], whereas fuel specifications and classes are delineated in the standard [4]. The latter is also stating origin of the biofuel, the traded form and a list of properties and classes for each biofuel. An additional standard [5] specifies the quality levels of theses classes, being in particular important for trading purposes.

With an annual consumption of more than 1.2 million tons of wood pellets in 2008 and up to 100,000 tons of straw pellets, Denmark belongs to one of the largest consumers of these types of biofuels in the world. More than one third of this amount is used in power plants for the generation of electricity and district heat. It is expected that use of biofuel pellets in power plants will increase from approximately 500,000 tons in 2008 to more than 2 millions tons in the near future [6]. Due to limited national resources, international trade is expected to increase rapidly and will require import of various types of biofuels from different international regions [27].

In other mainly northern European countries, the quantity of co-fired biofuel or pure biofuel combustion plants has also increased significantly over the last decade. Due to the CO_2 reduction targets in the Kyoto Protocol and the increased price levels of CO_2 emission permits (cap-and-trade) this trend is also highly noticeable internationally. A fundamental requirement for using solid biofuels as substitution or co-firing fuel for coal is that current coal-designed combustion technologies can be used with only a minimum of conversion in order still to be cost-effective. Different technical options for converting coal-fired power plants or using biofuels in a co-fired system exist and are extensively explained and analysed in the literature [7,32].

However, biofuels, especially wood and straw, also have certain drawbacks when considered as alternative fuels to coal, gas or oil, mainly attributed to their significantly higher heterogeneity, low energy density and high moisture content. These characteristics play a determining role for processing, combustion efficiency, transportation and of course, economically. Among other, this means that biofuels have to be pre-processed in such way that the specific coal-mills and furnaces, which have been designed for grinding coal and injecting the pulverized fuel into the furnaces, can continue to be utilized.

An important counteraction to the low energy density and the high moisture content of biofuels can be achieved by *pelletizing* biofuels (defined in CEN/TS 14588 as "densified biofuel made from pulverized biomass with or without additives"). The energy density of wood pellets for example can be five to six times higher than that of the raw material while moisture content simultaneously is reduced by up to 40% (w.b.). The increasing international trade, the demands on pre-processing procedures and combustion processes all require detailed knowledge of the inherent physical–chemical characteristics of biofuels.

Combustion standards, optimization processes, process- and monitoring efficiency are all strongly depended on proper quality assurance of the biofuel and raw materials, respectively. An especially important prerequisite for reliable quality assurance across the many and varied types of biofuels is a documented and valid procedure for extracting *representative samples*. Representative sampling is a critical success factor in order that biofuels can be precisely and accurately characterized, allowing reliable monitoring and quality assurance in the entire power generating sector. This review gives a critical assessment of all relevant sampling standards for solid biofuels and evaluates whether quality assurance can be said to have been ensured when applying the current standards.

2. Method of evaluation – Theory of Sampling (TOS)

The Theory of Sampling delineates all necessary principles for *representative sampling*, at *all scales* of interest, ensuring an *equal likelihood of all increments*[1] of the lot to be sampled. TOS has been developed over the last 60 years and has been applied to a wide

[1] TOS's specific terms are described in Table 1. "Increments" are almost never samples in their own right (grab sampling), but are destined to be aggregated to form a composite sample.

range of technical, academic and industrial sectors and applications. Based on a set of scale-invariant sampling unit operations, TOS also allows the analysis of representativity of all sampling methods, procedures and equipment types.

The most important factor, determining the importance of representative sampling, is the inherent *heterogeneity* of all naturally occurring materials at the full range of operative scales related to sampling. Lot heterogeneity makes sampling far from trivial and requires a solid understanding of both this phenomenon itself and, perhaps most important, how it can be *counteracted* in the sampling process. In fact all sampling processes disobeying the rules of TOS will create its own sampling errors, some of which are bias-generating (a fatal characteristic). Without specific qualification of the sampling process itself, it is not possible to determine whether a particular sample is representative or not. The effort towards representative sampling should therefore first be directed at analysing the sampling process conditions, in order to assess whether it can be guaranteed that the analyte concentration of a sample is acceptably close to the true average concentration of the lot. The specific sampling process errors, when not eliminated, will unavoidably result in an inconstant sampling-bias, which cannot under any circumstances be corrected for. Counteracting sampling bias is the first and foremost obligation for any sampling process – TOS has a quite specific term for this demand, "sampling correctness", see further below. The conditions for "sampling correctness" should be followed in every sampling standard and is therefore explained in more detail in the following.

For a complete introduction to TOS including the concept of heterogeneity, sampling unit operations, replication experiments, variography (process sampling) and other important aspects of TOS, the reader is referred to the selected literature [8–12,21,26]. Appendix A comprises a brief of the most central principles of process sampling, also including the sampling unit operations, since referred to in this article.

2.1. Representative sampling process

The Theory of Sampling sets forth a necessary set of fundamental concepts and definitions, which are provided in Table 1.

The fundamental sampling principle (FSP) stipulates the criterion for representativeness, requiring that all fragments in the lot should have the same none-zero probability of ending up in the final sample [8]. Elements not belonging to the lot must have a zero probability of being selected. The final sample should preferably be materialized by several increments from the lot, also referred to as 'composite sampling'. A unitary ("one scoop") sampling operation can never achieve sampling correctness, and therefore representativity, because the inherent lot heterogeneity is not counteracted in the sampling process.

A sampling process can only be representative, when a sample is extracted by a procedure that is both accurate and precise (reproducible) [8]. A sampling process is accurate if the average error (m_e), i.e. the difference between the analytical sample grade (a_S) and the analytical grade of the lot (a_L), equals zero or results in a predetermined acceptable low value, otherwise the sampling process is *biased*. Likewise a sampling process is precise (or reproducible) only if the variance of the sampling error (e) is less than a low predetermined value. Relative sampling error, accurate-, precise- and representative sampling process can expressed mathematically:

Relative sampling error: $e = (a_S - a_L)/a_L$
Sampling process accuracy: $|m_e| \leq m_0$ [m_0 is an acceptably, low predetermined level]
Sampling process precision: $\sigma_e^2 \leq \sigma_0^2$ where σ_0^2 is an acceptably low, predetermined value level
Representative sampling process: $r_e^2 \leq r_0^2$, where $r_0^2 = m_0^2 + \sigma_0^2$

Table 1
Fundamental concepts and definitions: Theory of Sampling.

Terms of TOS	Definition
Sample	Correctly extracted material from the lot, which only originates from a qualified sampling process (sampling correctness).
Sub-sample	Correctly mass-reduced part of sample (primary, secondary, etc.).
Composite sample	Aggregation of several increments – a composite sample represents "physical averaging".
Specimen	A 'sample' that cannot be documented to be representative.
Increment	Correctly delineated, materialized unit of the lot. Increments result from an aggregation process, while sub-sampling is a divisive process.
Fragment	Smallest separable unit of the lot, e.g. mineral grain, kernel, biological cell, etc. that is not affected by the sampling process itself. By naming the smallest unit-of-interest a fragment, TOS allows to treat even the situation in which the sampling process results in fragmentation of (some) of the original units.
Lot	Sampling target, e.g. truck load, railroad car, ship's cargo, batch, etc. Lot refers both to the physical, geometrical form as well as the material characteristics of the material being subject to sampling.
Lot dimensionality	TOS distinguishes between 0-, 1-, 2- and 3-dimensional lots. A 0-dimensional lot can be manipulated (forcefully mixed, moved, etc.) in its entirety without undue efforts.
Scale	Sampling efficiency is influential at all scales from increment to lot. Correct sampling is scale-invariant, i.e. the same principles apply to all relevant scales in the sampling pathway.
Heterogeneity	Heterogeneity is the prime characterization of all naturally occurring materials, including industrial lots. Heterogeneity manifests at all scales related to sampling for nearly all lot and material types. The only exception is uniform materials,[a] which is such a rare examples that no generalisation w.r.t. sampling can be made here from.
Sampling correctness	Elimination of sampling bias, by correct design, performance and maintenance of the sampling process/equipment. In the event of sampling correctness, only sampling precision remains, which is a much easier issue.
Representativeness	Representativeness implies both correctness as well as a sufficiently small sampling reproducibility.
Sampling bias	Systematic deviation between an analytical sampling result and the true average lot concentration, aka *accuracy*. Removal of sampling bias is the first obligation for any sampling process.
Reproducibility	Sampling variance, after removal of sampling *bias*, aka *imprecision*.
Process sampling	Process sampling is dealt with in Appendix A.

Source: [8,11,12,22,26].
[a] Uniform materials: materials with a repeated (correct) sampling reproducibility lower than 2%. Such materials do not occur naturally (exception gasses and infinitely diluted solutions, etc.)

The imperative nature of these concepts becomes obvious when evaluating grab sampling for example, a method that is widely used in practice and also suggested by many sampling standards (Section 4). Grab sampling refers to the process of obtaining samples (correctly called *specimens*) by unitary scooping from the lot.

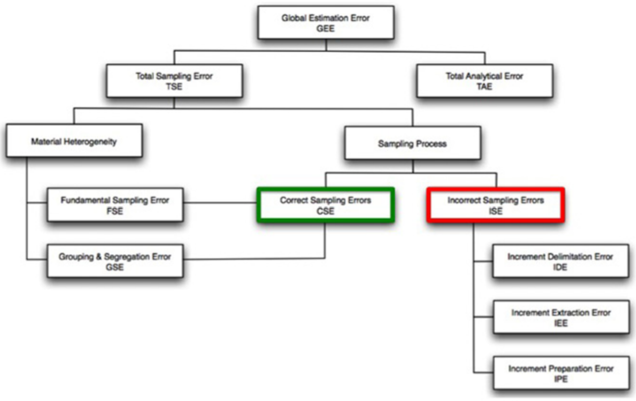


Fig. 1. Relation of TOS sampling errors in stationary sampling situations.

Since the fundamental sampling principle cannot be obeyed with this method, sampling is non-representative. Neither the grab sampling method, nor the many and varied types of equipment used for this procedure (spatula, scoop, shovel, front loader, etc.) can ensure accuracy and therefore neither reproducibility. Grab sampling is indeed the worst possible method of all since it always generates sampling errors, which can be up to hundredfold larger than the analytical error depending of the seriousness of the heterogeneity encountered. In order to ensure a representative sampling process sampling errors must be minimized or eliminated.

2.2. Sampling errors

Sampling errors, which are caused by incorrect sampling procedures, are termed 'incorrect sampling errors', whereas 'correct sampling errors' signify errors that are committed even when the sampling process is "correct". The following figure gives an overview of all sampling errors delineated by TOS, clarifying this differentiation (leaving out process sampling, see Appendix A) (Fig. 1).

Uncertainties of analytical results are expressed as the variance of the Total Analytical Error (TAE). All other sources of errors from sampling are aggregated in TOS as the Total Sampling Error (TSE). The sum of the TSE and TAE form the Global Estimation Error (GEE). For significantly heterogeneous materials, the Total Analytical Error (TAE) is usually of no practical concern as it is very nearly always significantly smaller than the sum of all sampling errors (typically 10–100 times smaller). The objective of representative sampling is to identify, minimize and eliminate all sources of the Total Sampling Error, which are caused either by the material heterogeneity or the sampling process itself – or both. The term correct sampling errors (CSE) comprises the Fundamental Sampling Error (FSE) and the Grouping & Segregation Error (GSE), both reflecting the material heterogeneity. In the Theory of Sampling heterogeneity is differentiated into constitutional and distributional heterogeneity. The constitutional heterogeneity (CH) describes the heterogeneity depending on the physical and/or chemical differences between individual fragments; CH increases when the compositional difference between fragments increases. CH is only dependent on the material properties. The error caused by CH is termed Fundamental Sampling Error (FSE), which can only be reduced by comminution (but never eliminated), therefore belonging to the correct sampling errors [8]. The Grouping & Segregation Error (GSE), the second correct sampling error, is due to the inherent tendency of particles to group and segregate. The distributional heterogeneity (DH) is dependent on the spatial distribution of the assemblage of all individual fragments or groups of fragments in the lot. GSE can only be reduced by the counteracting processes of mixing or decreasing the volume of the incrementing sampling tool [12,13].

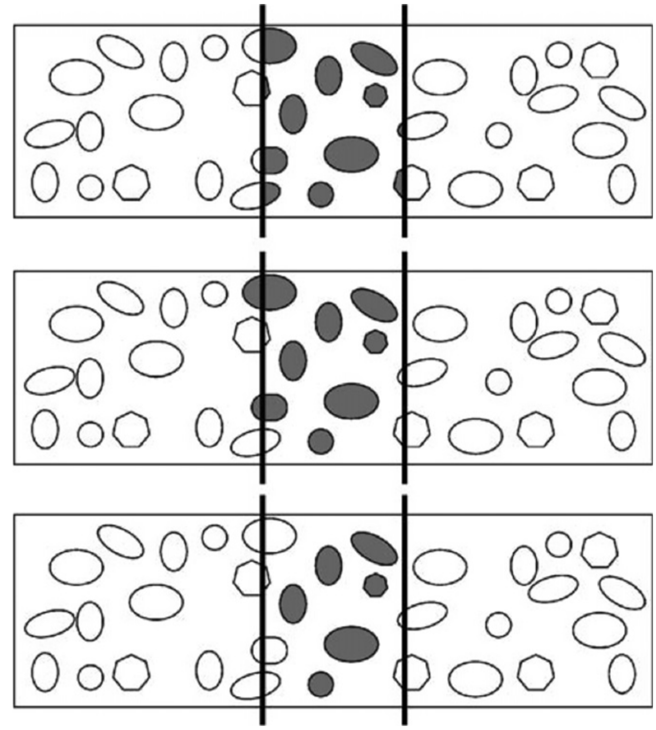


Fig. 2. Illustration of the *centre of gravity rule* with grey shadings demonstrating material, which must end up in the final sample, lest IEE occur. Upper figure: correct theoretical extraction. Center: correct practical extraction. Bottom picture: incorrect extraction, disobeying the centre-of-gravity rule.
Source: Gy, 1993; [9,11,13].

In contrast to the correct sampling errors, the incorrect sampling errors (ISE) must by all means be minimized, and preferentially eliminated, since these are the bias-generating sampling errors. If not eliminated by the design and operations in the sampling process, a fatal sampling bias is likely to result. Sampling bias cannot be corrected for by any post-festum procedure, data analysis, statistics or whatsoever. A sampling bias can only be avoided by a sampling process obeying TOS' principles for elimination of all incorrect sampling errors (ISE).

ISE comprise three error parts – Increment Delimitation/Delineation Error (IDE), Increment Extraction Error (IEE) and Increment Preparation Error (IPE), all concerning sampling equipment and sampling procedures.

The Increment Delimitation Error relates to the physical extraction of the increments. IDE can be avoided by delineating an increment that completely covers the relevant dimensions of the lot. A correct delineation of increments from lots forming a long pile of material (including moving material on conveyer belts) can be achieved by extracting a complete cross-sectional slice (1-dimensional sampling situation, see Section 2.3). The cutting planes defining the increment must be strictly parallel in both transversal and vertical dimensions, perpendicular to the process dimension. Two-dimensional sampling situations (Section 2.3) can be sampled e.g. by using a drill core to the very bottom of the layers [14].

The Increment Extraction Error occurs when particles inside the delineated increment do not end up in the sample, also referred to as the "centre-of-gravity rule", which states that fragments/particles having their centre of gravity inside the delimited increment should also end up in the final sample [8,11], as depicted in Fig. 2. Examples of IEE are particles bouncing off the sampling tool edges, fine particles that are blown away before extraction or

particles outside the delineated area entering the sampling tool and therefore leading to contamination.

The Increment Preparation Error (IPE) arises when increments/samples are altered after extraction, e.g. suffering contamination, evaporation, moisture absorption, loss of material (spillage), and including also deliberate manipulation (fraud or sabotage). Correctly sealing and storing of final samples is of course a must in order to limit potential IPE.

In many instances elimination of incorrect sampling errors requires only minor, but decisive and critically needed, changes to an existing sampling process – at other times the sampling process itself is so compromised by faulty design (or operation, or poor maintenance) that fundamental changes are needed. It is always crucial, without exception, that ISE are eliminated in all primary, secondary, etc. sampling and mass reduction procedures. Observe that this demand is scale-invariant. Sampling bias can occur at all operative scales. Since the main purpose of sampling standards is to standardize sampling equipment and procedures that ensure representative sampling and mass reduction, none of these error sources should be allowed by the descriptions and recommendations in any sampling standard and are therefore the fundamental basis for the standards' review part of this paper.

2.3. Lot dimensionality

In TOS lot dimensionality is not only related to the physical geometrical aspect of the lot (e.g. stockpile, material on conveyer belt, etc.) but rather refers to the operative number of dimensions to be covered during the sampling process. The concept of lot dimensionality becomes clear when considering an elongated material stream. Using grab sampling as an extraction method, the source stream must be considered 3-dimensional, since grab samples are most likely only taken from the top surface part of the moving flux of matter. However, by applying a *cross-stream cutter*, which allows to extract any number of correctly delineated increments consisting of material from the entire depth and width of the source stream, the sampling situation is reduced to one dimension: the only decisive dimension is now the longitudinal dimension of the matter stream. TOS considers 0-, 1-, 2-, and 3-dimensional sampling lots. The special case of a 0-dimensional lot refers to a lot that can be effectively mixed, manipulated, moved and sampled throughout with complete correctness. 1-dimensional lots refer to sampling situations for which one dimension in space dominates (e.g. conveyer belts, process streams, pile lines, etc.) and present the optimal sampling situation according to TOS (for more coverage of process sampling, see Appendix A). For 2- and 3-dimensional lots, two or three dimensions are dominating in the same sense. Whenever possible these lots should be reduced to a 1-dimensional sampling situation [8,11]. This stipulation is called "lot dimensionality transformation", and is but one example of a total of seven sampling Unit Operations (SUO), which has been promulgated (see Appendix A).

3. Sampling standards – the CEN scene

All member states of the EU are obliged to establish a national standardization institute to enforce standards developed by the CEN, implying that national standards in conflict with CEN standards are not permitted. While CEN standards are still declared as pre-standards or as CEN/TS (Technical Specifications), national standards can still exist in parallel. Technical Specifications (TS) have to be upgraded to a full CEN standard or deleted after three years. For subjects that are not covered by any CEN standard, use of national standards is allowed.

For the following evaluation of biofuel sampling standards this *modus operandi* of the European standardization system is decisive for setting the scope of the review, which focuses on assessing whether the standards fulfil all necessary criteria for representative sampling. The primary concern is that standard(s) must be based on sufficient TOS-competency in order that overviews, descriptions, illustrations and recommendations are not fraught with *incorrect sampling errors* (not only allowing, but *guaranteeing* sampling bias) and at least a modicum of elements for reducing *correct sampling errors* as well [10,15].

CEN has published three standards regarding methods for sampling [16], sample preparation [17] and sampling plans/certificates [18] for solid biofuels. In particular the standards for sampling methods and sample preparation are in focus here, since they dealing directly with the practical issues of sampling.

[19], which deals with sampling of pulverized coal conveyed in circular pipes by air (or other gases) is also evaluated. Even though this latter standard was originally set up for pulverized coal, it is stated in the standard that it does not preclude from being suitable for sampling other pulverized materials as well. This sampling standard is important when dealing with pelletized biofuels that are co-fired in conventional or solely fired in converted coal power plants. The fuel combustion process requires that these biofuels are also pulverized and transported by pressurized pipes to the burners. Correct sampling in pressurized pipes is crucial for a reliable determination of the final fuel characteristics, whether coal or biofuel dust.

4. Evaluation

4.1. Evaluation of primary sampling standard for solid biofuels

Solid biofuels [20] part 1 and part 2 define methods for sampling solid biofuels across the entire scene from the location where the raw materials grow, from processing plants, from transportation pathways and deliveries and from various types of stock. Both manual and mechanical methods are included. These standard are stated to be valid for solid biofuels that are either:

- "Fine and regularly shaped particulate materials, particle sizes up to about 10 mm that can be sampled using a scoop or pipe, for example: sawdust, olive stones and wood pellets;
- coarse or irregularly shaped particulate materials, particle sizes up to about 200 mm that can be sampled using a fork or shovel, for example: wood chips and nut shells, forest residue chips, and loose straw;
- baled materials that require a special sampling tool to be used if the bales are not to be broken open for sampling, for example: baled straw or grass;
- large pieces (particles sizes above 200 mm) which are to be picked manually;
- fibrous and vegetable waste dewatered in belt press" [16].

Focussing on wood and straw pellets as the solid biofuel intended for extensive use in converted coal power plants, the first category sampling of 'fine and regularly shaped particulate material' is particularly relevant in the present analysis (always bearing in mind that TOS' principles are generic and scale-invariant). Table 2 gives an overview of the evaluation results with respect to potential TOS-incorrect sampling errors caused by the methods stated, recommended or allowed in the standard for primary sampling methods (CEN/TS 14778).

Table 2
Potential incorrect sampling errors of primary sampling methods stated in CEN/TS 14778.

	IDE	IEE	IPE
Three-dimensional lot	**Sampling from stationary lot**		
	High error potential	High error potential	Medium error potential
One-dimensional lot	**Conveyer belt**		
Manual sampling (stopped conveyer belt)	High error potential Low error potential	Medium error potential	Medium error potential
Automatic sampling	High error potential Low error potential	High error potential	Medium error potential
One-dimensional lot	**Falling source stream**		
Manual sampling	High error potential	High error potential	Medium error potential
Automatic sampling	High error potential Low error potential	High error potential Low error potential	Low error potential

4.1.1. *Sampling from stationary 3-dimensional lots*

Stationary lots, defined as zero-, 1-, 2- and 3-dimensional sampling situations, comprise the toughest challenge for sampling. Zero-dimensional lots are, by definition, easily sampled in complete correspondence with TOS. Also stationary 1- and 2-dimensional lots are relatively easy to tackle, as the necessary TOS principles, procedures and equipment can be brought to bear on the heterogeneity issues [8–12,21,22,26] – but a minimum of TOS understanding and determination to implement the necessary modifications in existing sampling procedures must of course be present. For the case of process sampling (dynamic 1-dimensional lots), referral is made to Appendix A. Significantly large, heterogeneous 3-dimensional lots are typically not feasible for correct sampling, unless sometimes drastic measures can be put into play, often an economically or logistically prohibitive approach (e.g. forceful mixing of the entire lot). However, nearly all such sampling is eminently possible, not only in theory but also in practise – transformation of lot dimensionality, in this case from a (stationary) 3-dimensional lot to a (dynamic, or stationary) 1-dimensional lot is the universal operative counter approach, which has helped greatly in innumerable sampling situations (SUO 1, Appendix A). The literature is ripe with an overwhelming number of illustrative examples and complex, difficult case histories, which only succeeded in producing representative samples because of SUO 1.

Unfortunately however, this important prerequisite for correct sampling is only mentioned in passing in standard CEN/TS 14778-1, which states that sampling is “easier when the material is moving” and should therefore “be preferred wherever possible”. This is far from a satisfactory TOS understanding and very far from achieving the maximum effect of an international standard. By not making much more explicit the negative effect of e.g. grab sampling in this and similar situations, there is a significantly increased uncertainty on the validity of the sampling procedures allowed for. The methods for sampling stationary lots will therefore in the best case lead only to a very rough approximation of the true concentration of the lot, due to the unwitting, but allowed (indeed recommended) *high potential for incorrect sampling errors* and hence to a very likely sampling bias. Thus, the standard actually mentions sampling tools for stationary lots like scoops, pipes, shovels and forks, which are de facto termed ‘unbiased mechanical equipment’. This is in blatant disagreement with reality [8–12,21,26], and in fact raises a very high potential for causing IDEs and IEEs. Increments produced by these types of implements will neither be correctly delineated, nor is ensured that material located within the boundaries of delimitation is actually extracted (e.g. differential spillage opportunities abound). Due to the fact that these extraction techniques do not give an equal probability for each particle to be sampled, also the fundamental sampling principle is disobeyed.

Evaluating the case of sampling wood pellets from stationary lots, the standard also gives fatal room for personal judgement by classifying wood pellets as a “homogenous biofuel”. This recommendation to visually inspect the lot whether it consists of substantially different material, invariably opens up a possibility to conclude that the fundamental sampling principle does not need to be applied for these kind of biofuels since dealing with ‘homogenous’ materials. Inspection of a stationary lot at a certain distance, might indeed lead to the impression that all constituents *appear* identical, but just by moving closer to the lot visual differences from some parts of the lot to another may be observable. The heterogeneity of the material will be certainly obvious when moving down to the level of each fragment. Fragments will in practice never be strictly identical (homogenous); different composition, shape, density, size, etc. occur. Above all however, most chemical and physical fuel parameters cannot be observed by the human eye. The stated classification of wood pellets as homogenous in the standards is wrong.

The assessed medium error potential for IPE is caused by the non-covered mechanical equipment types as well as subsequent free decanting of increments into a composite sample, which both might lead to loss/gain of material. The standard states however that the combined composite sample “can be placed in air-tight packages such as plastic buckets (with lids) or plastic bags (to be closed)”. Needless to say that this of course should not be an option but a mandated precaution against IPE.

4.1.2. *Stationary 1-dimensional lot: manual sampling from stopped conveyer belts*

CEN/TS 14778-1 differentiates between automatic vs. manual sampling from conveyer belts and falling source streams, both 1-dimensional sampling situations according to TOS.

The first scenario concerns manual sampling from stopped conveyer belts. The suggested use of a sampling frame for extracting increments is very good and can easily ensure a correct delineation of increments, provided that the dimensions of the frame cover the entire width and depth of the conveyer and the cross-section of the increment are designed as two parallel planes. Depending on this, the potential for IDE can vary between high (not designed according to TOS) and absent/low (correctly designed). The standard is not defining any of the required prerequisites for eliminating the possible IDE, and is therefore depending on the competence of the OEM – and less on the sampler’s knowledge about representative sampling. This scenario is almost universal: there is often an overwhelming faith placed in that “the equipment will carry the day” – and it is not considered with sufficient understanding that even correctly designed equipment can be used in a non-representative manner. Regarding the opening dimensions of the sampling frame the standard states correctly according to TOS that it should be at least 2.5 times the nominal top size of the material to be sampled, limiting the potential of an IEE (we here refrain from commenting to harshly that this should be defined by a factor: $3+\varepsilon$ according to TOS). The conditions for minimizing/eliminating of IEE are however compromised by subsequently stating that in the case of

trapped material under the edges of the sampling frame "the material trapped under one edge shall be included in the increment and the material trapped under the other edge shall be excluded from the increment" (CEN/TS 14778-1). This additional selective operation can increase the IEE potential (declared as medium error potential in Table 1), allowing that including or excluding trapped material is no longer subject to an objective selection process.

The medium error potential of the IPE is caused by the same reasons as explained for sampling of 3-dimensional lots.

4.1.3. One-dimensional lot: automatic sampling of conveyer belts

For automatic sampling of conveyer belts the standard suggests a cross-belt sampler. It is correctly defined that the device must be able to extract material from the full depth of the conveyer. This design requirement raises many practical difficulties, as pointed out in an extensive TOS analysis [23]. This author even recommends that cross-belt samplers "should be rejected in sampling standards, because too many problems remain unresolved, which raises many concerns about the compliance to the rules of sampling correctness" [23]. The main problems Pitard has analysed are stated in the following.

The necessary gap between conveyer belt and sampling cutter, which is required in order to prevent damages of the conveyer belt does not allow to cover the full depth of the conveyer. A brush installed at the back of the cutter intended to sweep up fine material that remains on the belt after trajectory across the stream, does also not necessarily lead to a full recovery of the delineated material. Some material will likely go sideways, leading to the stated high potential for an IEE. Also such brushes are sure to wear down very quickly and need an extremely careful and timely maintenance schedule.

Furthermore the capacity of the cross-belt cutter must be compatible with the flux of material on the conveyer belt. Additionally the velocity of the cutter is decisive. While conventional cross-stream samplers, which will be discussed when analysing the standardized methods for sampling falling sources streams, should have a maximum cutting velocity of about 45 cm/s, this rule does not apply to cross-belt cutters. Pitard states that the faster the cutter crosses the stream on the conveyer belt the more likely it is going to do a good job [23]. However, high velocity raises the problem that material located on the upstream of the cutter is pushed into the collected increment, increasing an IEE potential (Pitard, *pers. com.*, 2010).

None of these problems are stated in the standard, neither it is mentioned that cross-belt samplers must also cover the entire width of the belt, ensuring that the increment consists of a full cross-section defined by two parallel (or curvy-parallel) planes. Use of this standard, which does not consider these requirements will allow for a very high risk for IDE and IEE. A low potential for IDE can only be guaranteed if the sampling device delineates samples in complete compliance with TOS.

The required high velocity of the cross-belt sampler might also cause that material bounces back on the conveyer leading to a loss of material. Based on the assumption – not explicitly stated in the standard – that the extracted increments are automatically collected in a closed system to combine the composite sample the total IPE potential is rated as medium, since at least at this stage loss or contamination of material is prevented.

4.1.4. One-dimensional lot: manual sampling from falling source streams

According to the standard falling source streams can be either sampled manually or mechanically. For manual sampling the standards states to use a sampling box or other suitable equipment that ensures an extraction of the entire cross-section of the falling source stream. Even though width and depth of the manual sampling device are correctly defined (depth is only vaguely specified: "box shall be large enough so that it does not become overloaded" (CEN/TS 14778-1)), a manual sampling can under no circumstances ensure a constant velocity of the sampling device passing the stream, therefore obeying the fundamental sampling principle. This causes a high potential for incorrect delimitation and extraction. The assessed medium potential of an IPE is mainly due to the suggested manual pouring of the increment for creating the composite sample. This procedure is significantly at risk to suffer a loss of fine particles.

4.1.5. One-dimensional lot: automatic sampling from falling source streams

The method for automatic sampling from falling source streams is standardized in exactly the same way as for sampling the source stream manually, only specifying dimensions and velocity of the cross-stream cutter. According to TOS and Pitard's [11,23] detailed analysis of the gamut of current sampling devices, such specifications for automatic cross-stream sampling are not sufficient and will result in a variable, but never eliminated potential for IDE and IEE. There are a plethora of possibilities for both correct as well as incorrect equipment designs, which are not addressed by the standard, again leaving the user at the mercy of OEM TOS competency. From extensive experience (WCSB1-5[2]) there will be all manner of different low, to medium, to high potential risk for significant incorrect sampling errors (IDE, IEE).

Under the assumption that increments and composite samples are handled in a closed system, the potential for IPE can be minimized. For a detailed list of TOS-correct design specifications of cross-stream samplers limiting IDE and IEE, the reader is referred to the doctoral thesis of Pitard [23], discussing cutter design, driving force and velocity of cutter, discharge mechanism and criteria for maintenance.

Before evaluation of the CEN sampling preparation standard (CEN/TS 14780), the suggested sampling intervals for dynamic 1-dimensional sampling situations will be briefly discussed. For all 1-dimensional sampling methods the standard declares that increments shall be taken at regular intervals during the discharge of the lot or sub-lot. Industrial 1-dimensional lots are often generated by chronological operations, as it is also the case for the combustion of wood and straw pellets (transportation from silos, grinding, transportation of pulverized biofuel, combustion). In addition to small-scale fluctuations, mainly due to the heterogeneity of the material, thus also periodic fluctuations can exist. Periodic fluctuations (long-range and cyclic) are mainly due to variations in certain process steps and require special observation [8,10,22].

Knowledge of periodic fluctuations can help to optimize certain process steps, reducing the variability of the product. By implementing regular fixed sampling intervals (also termed 'systematic' in TOS) the risk exists that samples are extracted with the same frequency as such possible periodic fluctuations occur, in which case these fluctuations will remain uncovered in the ensuing analysis. Gy suggests that for 1-dimensional lots, a *stratified random* sampling interval should always be available, which will unlock any correlation with the presence of such cycles [23]. Stratified random interval means that within a certain time frame (e.g. within every 5 min) an increment is extracted at a randomly selected time. Process sampling is treated in full in Appendix A.

[2] WCSB; World Conference of Sampling and Blending. Bi-annual conference for professional samplers, scientists, technology, industry – inaugurated in Denmark 2003.

4.2. Evaluation of sample preparation standard for solid biofuels

The main purpose of sample preparation is to reduce a sample, very likely a sub-sample from a previous primary (or secondary) sample, to the required analytical sample size. Typically mass reductions of the order of 1:1000 to 1:100,000 have to be invoked from primary sample to analytical aliquot [8,9]. All intervening mass reduction method must therefore be in full compliance with the fundamental sampling principle [15]. The universal requirement is that all TOS' principles are honoured across all scales, across all sampling and preparation stages. All manner of operations of the type "sample preparation" and "sample handling" must be seen as parts of the entire sampling scale hierarchy (sample preparation always involves *some measure* of sub-sampling, etc.).

These prerequisites for correct mass reduction according to TOS are also stated in the CEN standard for sample preparation for solid biofuels – CEN/TS 14780. The standard also describes different particle size reduction methods. The Increment Preparation Error (IPE) is the sole potential ISE for these particle size reduction methods. In compliance with TOS, the standard states that particle size reduction equipment like mills or crushers must be designed in a way that loss of material and contamination of the material is prevented, by using closed and easy to clean systems. It also states correctly that if the material shall be analysed for its moisture content, care must be taken to avoid any significant heat build-up and risk of drying (CEN/TS 14780). The methods for determining moisture content are standardized in EN 14774:2009 [28–30].

In the following the different mass reduction methods are evaluated. According to the standard the 'correct' mass reduction method has to be selected, which depend on the minimum masses retained during the mass reduction stages. This in return is stated to be based on nominal top size and bulk density of the material. If these characteristics are known before a final analytical sample has been derived and analysed for these characteristics, this approach is insufficient, and if not, a simple pilot survey will suffice. The standard describes mass reduction methods that should be used for initial sample reduction, for reducing material smaller than 30 mm and for material smaller than 1 mm.

Petersen et al. have performed a comprehensive survey of almost every current mass reduction principle, procedures and hardware for different materials and concentrations, quantitatively characterizing the methods and instruments for accuracy, reproducibility, material loss, user-dependency and operation time [9]. Their results have been applied to the mass reduction methods of the present standard, as depicted in Table 3. For evaluation of the mass reduction method 'coning and quartering' the results of the study performed by Gerlach et al. was consulted [24], while for "strip mixing" (laboratory scale bed blending) results from Wagner and Esbensen [14] were used, as both these techniques were not considered in Petersen's study. The following mass reduction methods are listed according to the order of appearance in the standard CEN/TS 14780.

Table 3
Assessment of mass reduction methods approved in CEN/TS 14780.

Standardized Method (CEN/TS 14780)	Ranking [9,24]	
Initial sample reduction		
Coning and quartering	Poor	
Riffling (>16 slots)	Acceptable	Very good
Strip mixing (bed-blending/multi-increment reclaiming)	Very good	
Long Pile (fractional shovelling)	Poor	
Manual increment division	Poor	
Rotary divider	Acceptable	Very good
Mass reduction of material < 30 mm		
Handful sampling	Poor	
Coning and quartering	Poor	
Riffling (>16 slots)	Acceptable	Very good
Strip mixing (bed-blending/multi-increment reclaiming)	Acceptable	
Long Pile (fractional shovelling)	Poor	
Manual increment division	Poor	
Mass reduction of material < 1 mm		
Extraction with spatula	Poor	

Coning and quartering is suggested by the standard "for materials such as sawdust and woodchips that can be worked with a shovel" reducing the sample mass down to approximately 1 kg (CEN/TS 14780). The principle behind this method is that the sample is mixed and subsequently arranged into a flattened pile, subsequently divided into four "equal" quadrants and repeated on two opposing quadrants until the required reduced sample mass is reached. Some method specifications even allow further sub-division to be based only on one quadrant, for which the *critique* below will be even more severe. From even the most casual TOS understandings, it will be highly evident, that the Grouping and Segregation Error (GSE) potential will be alarmingly high (in a mostly uncontrollable way) for this method, which in general will lead to (very) poor results with respect to representativeness, as everything will depend on the effectiveness of the preceding mixing, a point almost universally not emphasized enough. In numerous descriptions of this approach there is a fatal lack of understanding of the need for this maximum GSE-reducing efficiency, in which the critical need for "mixing" being maximally thorough is barely mentioned. Irrespective of the initial mass or size of material, coning and quartering cannot under any circumstances be recommend as a representative mass reduction method, compare [24].

Riffle splitting is one of the most well founded mass reduction methods, although it neither guarantees completely fail-safe results. In order to function correctly, certain principles according to TOS need to be considered. The main principle states that the sample must be filled into a rectangular area, divided by an equal number of parallel, identically dimensioned chutes leading to two separate receptacles. The higher the number of chutes, the better the sample is split. Depending on the particle size, the width of the chutes must have certain size, strictly larger than three times the nominal top size of the material, in order to prevent blocking or bridging [9,25].

Besides these design requirements of which the standard only refers to the number of chutes (at least 16) and width of chutes ($3 + \varepsilon$ times the nominal top size of the material), also the handling of the riffling device is essential for obtaining a representative mass reduction. The sample must be spread out equally over the whole length of the feeding tray, which must have exactly the same width and length as the rectangular receiving region of the splitter, preventing that particles bounce out the receiving tray. Additionally the 50% split sample, used for further mass reduction or analysis, must be selected at random. The handling procedures are sufficiently stated in the standard with the exception of the random selection, which is not mentioned. Due to limited design prerequisites and incomplete handling advices, the riffling method in CEN/TS 14780 is ranked as acceptable/very good, depending on whether all or only the stated requirements of the standard are fulfilled.

4.2.1. Strip mixing (small-scale bed blending)

Strip mixing (bed-blending stacking/multi-increment reclaiming) can be appreciated considering the following figure and the practical example shown in Fig. 4.

The sample is laid out in a multiple layering stacking operation in as many layers as possible; this procedure is termed

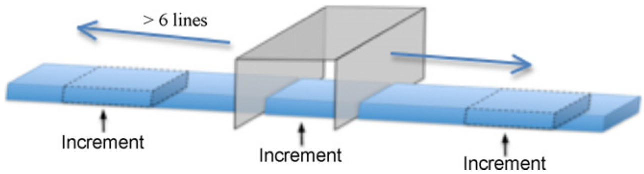


Fig. 3. Method of strip mixing (bed-blending/multi-increment reclaiming).

bed-blending in the technical literature and is a particularly efficient form of mixing. Increments are subsequently extracted by inserting two parallel plates (or an extraction device with the same design requirement) vertically into the layered stack, removing all material from in-between the plates. The procedure is comparable with stopped conveyer belt sampling. In direct proportion to the number of stacked layers (P), this reclaiming extracts P equidistant increments simultaneously, already aggregated into a composite increment. Using several such "super-increments", see Fig. 3, amounts to a truly extraordinary thorough composite sampling. It is clear that effectiveness hinges critically on the preceding mixing.

The standard suggest to take at least 20 increments from evenly spread locations, making the total effective number of increment equal to $20 \times P$; it is difficult to conceive of a more efficient mixing-and-reclaiming method. The width between the plates is not defined and can therefore be chosen according to the required mass reduction specification, subject to the standard requirement of being at least three times larger than the nominal top size of the material. The strip mixing method as described in the mass reduction standard, can be therefore rated as very good.

The methods **long pile** and **manual increment division** can be characterized as *shovelling methods*. The long pile approach is a combination between strip mixing and fractional shovelling. The sample is laid up in a single, or multiple 1-dimensional stack, which is subsequently split in the required number of subsamples using a shovel. The standard states that each subsample should consist of at least twenty shovelfuls.

The manual increment division method is stated to be suitable for sawdust and other biofuels with small particle sizes. The sample is 'homogenized' by mixing it with a scoop before spreading the sample into a rectangle with a thickness of not more than three times the nominal top size of the material. Subsequently the rectangle is subdivided into at least 20 parts from which each a sample is taking by using a scoop. Both, these standardized shovelling methods have been ranked as poor, since major IDE and IEE errors are unavoidable. The use of a shovel can neither insure correct delineation nor extraction of the increments. Even though the long pile method (modified fractional shovelling) could be ranked as slightly better than the manual increment division method, criteria as mass equality, composition, user-dependency and poor efficiency make this method unsuitable as a representative mass reduction method.

Rotary dividers (also termed revolving splitters) are based on the same principles as riffle splitters. Rotary dividers distribute the sample mass equally over a number of radial chutes, thereby ensuing a sample split ratio according to the number of chutes. The only design requirements stated by the standard are that the divider rotates at least 20 times while the sample is being divided and that the chute size should be at least 2.5 times as wide as the nominal top size of the material to be processed. Due to the limited design requirements of the standard, the validity of the mass reduction is strongly dependent on the correctly designed rotary divider, this method has been ranked as acceptable/very good. The typical very equal splits (if correctly designed) and factors like short handling time and user independency led to the very good ranking of rotary dividers in Petersen's et al. study.

For materials smaller than 30 mm the standard states that also **handful sampling** can be applied. This alternate shovelling is based on the same method used for manual increment division with the difference that the sample is divided into two piles using the hands as a sampling tool. Needless to say that this grab sampling method cannot lead to a representative mass reduction, due to incorrect delineation, extraction and the potential for very high individual variability.

Similar problems occur at the lowest scale of sampling interest when extracting subsamples with a **spatula**, which is stipulated as the only mass reduction method for materials smaller than 1 mm in the standard. A spatula used to take out the required quantity in one scoop is of course identical to grab sampling, and as such is disregarding several key TOS principles. The standard does mention that in case of impurities "care must be taken especially for the segregation of particles", but without clear descriptions on what to do. Spatulating is a method that in almost all cases is distinctly inferior and insufficient and is therefore here rated as poor. Only in the case of fully documented acceptable pre-mixing can grab sampling with a spatula be considered. Esbensen et al. described a method for such qualification, termed a *replication experiment* [26].

It is obvious that spatulating is but one example of grab sampling. It is again the degree of mixing, which is the deal-breaker in all such cases; this understanding is scale-variant (as a crass example, taking a "sample" with a front-loader with a one-ton scoop at a municipal waste depot... is still grab sampling).

4.3. ISO sampling standard for pulverized material

In many converted coal power plants, solid biofuels are pulverized and pneumatically transported to the burners, for which reason this review evaluates ISO 9931 – sampling of pulverized coal conveyed by gases in direct fired coal systems. Even though

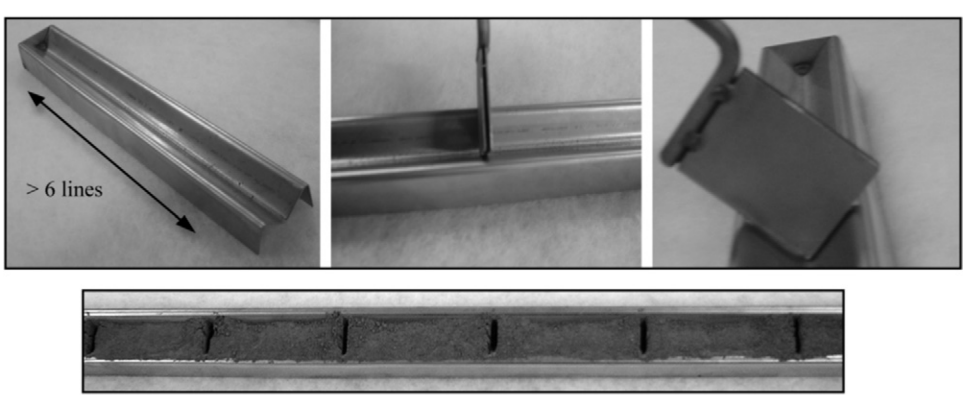


Fig. 4. Practical example of strip mixing for extracting analytical sample sizes.

Table 4
Potential incorrect sampling errors of ISO 9931 sampling method.

	IDE	IEE	IPE
One-dimensional lot	**Multipoint sampler**		
	High error potential	Low error potential	Low error potential
		Medium error potential	Medium error potential

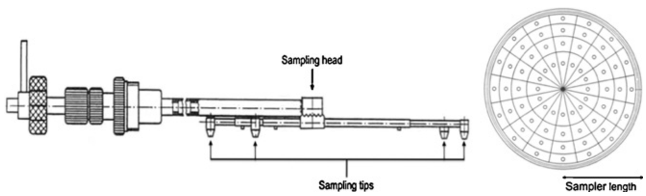


Fig. 5. Multipoint sampler according to ISO 9931 (left figure), sampling positions (right figure).
Source: ISO 9931, modified by the authors.

originally specified for pulverized coal, it is stated that the standard can also be used for sampling of other pulverized materials. The scope of the standard is limited to the following specifications:

- Only vertical circular pipes can be sampled with an internal diameter between 250 mm and 700 mm.
- The maximum particle size is less than one-third of the diameter of the sampler opening.
- The air/coal (material) ratio in the pipe is within the normal range of direct fired pulverized coal systems.

The standard's principle for extracting a representative sample of pulverized material in a vertical flow is based on a multipoint sampler. The multipoint sampler, as depicted in the left figure below, is equipped with four sampling tips through which increments can be extracted simultaneously. The sampling tips are attached to the sampling head allowing a rotation in concentric circles (Fig. 5).

The standard claims that the radial positions of the four sampling tips and the use of equal time sampling with the sampler set at 16 angular positions ensure sampling from equal areas of the cross-sectional area of the pipe (see right figure). In a time frame of 4 min a sample is extracted from 64 sampling points (4 sampling tips $\times$ 16 angular positions) evenly distributed over the cross-section of the vertical pipe. The multipoint sampler is inserted through a dustless connection into the pulverized flow. During insertion, the intrusion of particles into the sampling tips should be avoided by continuous back blowing. Once inserted the sampler is switched from back blowing to suction with an extraction velocity that should be 1.1 ± 0.1 times the mean gas velocity in the pipe. After every 15 s the sampler is switched to the next sectoral position, until all 16 positions have been covered. The extracted material is sucked into a sample bottle and sealed with an airtight lid. In order to avoid cross-contamination between different sampling operations, the multipoint sampler should be cleaned after each sampling operation by using the back blow function.

The standard also defines the sampling positions, stating that the minimum distance from an upstream disturbing component should be at least five times the internal diameter of the pipe. In the presence of a downstream disturbing component, the distance of the sampling position should be at least equal to the internal diameter of the pipe.

Table 4 shows the rating of the incorrect sampling error potentials according to TOS of the described multipoint sampler.

The main error potential is caused by incorrect delimitation of the sample. The multipoint sampler, as implied by the name only covers fixed points and not the entire cross-section of the source stream, meaning that not all particles have an equal chance of ending up in the sample. Furthermore by switching the sampler to the next sectoral position with a time delay of 15 s and a total required time of 4 min, the composition of the cross section may very well vary in the corresponding longitudinal pipe segment. This should

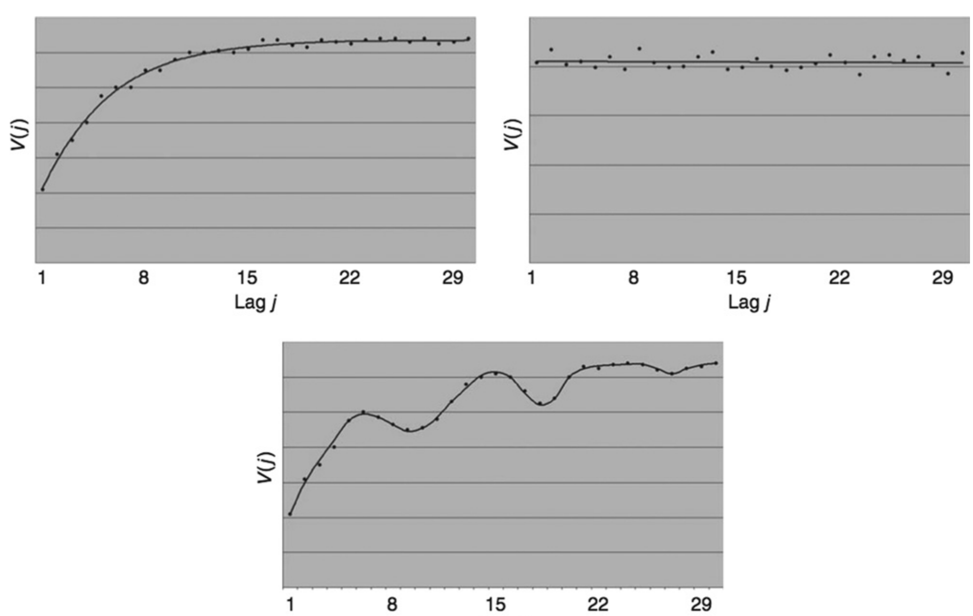


Fig. A.1. The three basic variogram shapes.

Source: [22].

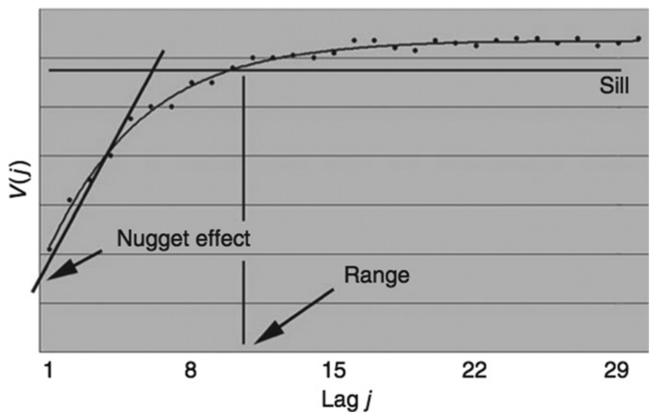


Fig. A.2. Generic variogram, schematically defining the nugget effect, the sill, and the range.
Source: [12].

not be mistaken with extraction of time-delayed increments that are combined to a composite sample, since each increment must cover the entire source stream, the entire cross section in this case. Furthermore the only vaguely explained distance of the sampling positions away from disturbances or horizontal distances that in return can lead to segregation is not sufficient. Despite this principal very strict critique, in practice this sampler stands a reasonably good chance to collect somewhat acceptable working composite samples.

There is one remarkable mistake of significant proportions perpetuated in this standard however, which merits a magisterial comment: the standard recommends that sampling positions should be established in similar places and at the same distances from disturbance components, in order "to get the same bias" for each of the sample. However, since the bias is caused by the incorrect delimitation and extraction from a heterogeneous material, a sampling bias can never be constant; sampling biases are never constant. This is one of the most often met with misunderstandings in what could be called "casual sampling incompetence", completely without foundation in reality. It is a lucky coincidence that this major flaw did in fact not influence the design of the basic operations of the multipoint sampler's ability to produce composite samples with a high likelihood for acceptable averaging. Thus in respect to IEE and IPE, the multipoint sampling procedure can be rated as good (low error potential), to satisfactory (medium error potential), since extraction of sample and storage are handled according to TOS.

5. Conclusion and prospects

Assessment of all sampling procedures of both relevant sampling CEN standards for solid biomass and of the ISO standard for pulverized materials shows that most of the recommended procedures do not lead to fully satisfactory result, a representative sample. Correct delineation and extraction of many standardized methods as well as depicted tools and equipment is not ensured. While for grab- and shovelling methods correct delineation and extraction is hardly ever possible, other recommended sampling methods lack sufficient specification, which invariably increases the potential for incorrect sampling error effects. Only two methods – riffling splitting and the rotary divider – allow good quality assurance of the representativeness. Again the analysis shows that grab- and shovelling techniques do not give assurance for representative mass reduction.

Insufficient specifications and existence of incorrect sampling errors must under all circumstances be eliminated in sampling standards as the result is an inconstant sampling bias, out of control. Incorrect sampling methods, room for personal interpretation and the vertical standardization approach of CEN and ISO, specifying different procedures for each material group, makes sampling a complicated issue with a highly uncertain and varying validity. Any procedure and standard that has not eradicated all potential sampling bias does not comply with TOS' stringent and demands for sampling correctness. The result is always unacceptable.

Full competence with TOS is a non-negotiable requirement for formulating valid sampling standards.

It should be noted that currently a new draft that if accepted will supersede CEN/TS 14778-1 and 2 from 2005 has been submitted to the CEN members for acceptance procedure. This draft, dealing with sampling methods of solid biofuels cannot be revised in this article due to the current approval phase. It can however be stated that some of the critical points of standard CEN/TS 14778 raised in this review have been improved to a certain extent in this draft. In particular by stating potential error sources of certain sampling methods, the sampler's awareness of potential error sources should have become somewhat more sharpened by this review.

Nevertheless the draft still carries all the sampling methods reviewed above (sic), which of course can still not be rated as representative according to the Theory of Sampling. Samplers, which are not aware of the imperative of *correct* delineation and extraction of increments, will still be allowed to use "recommended" methods like grab sampling or shovelling, which, as shown above, can never lead representative samples or to representative mass reduction.

In order to avoid a multitude of standards for different material groups, currently a horizontal sampling standard is in working progress. The main benefit from horizontal standardization is the advantage to apply one, unified sampling standard to almost all types of lots and materials. In order to achieve this wide applicability, the principles of representative sampling must be come to the fore, rather than focussing on different sampling equipment. The new horizontal sampling approach will be in full appliance with the fundamental principles of the Theory of Sampling.

The increasing use of and international trade with biofuels demand that quality assurance must be ensured for all trading-, process- and monitoring stages. Only representative sampling as defined by TOS allows reliable, valid determination of the relevant characteristics for loads, stockpiles and source streams of various biofuels and their raw materials and must be therefore integrated in all current and future sampling standards.

Appendix A. Process sampling – 1-dimensional lots

One-dimensional lots refer to sampling situations for which one dimension in space dominates, whereas the other two dimensions are negligible in size compared to the third dimensions; 1-dimensional lots present the optimal sampling situation according to TOS. 1-dimensional lots can be subdivided in three different kinds [8,11–13,15,31]:

- Moving or stationary stream of particulate material (e.g. conveyer belts)
- Moving or stationary string of fluids (e.g. fluids in pipelines)
- Moving or stationary stream made of discrete chronological units (e.g. truck loads, units like bags, packages, etc.)

One-dimensional lots are characterized by increments being compositionally correlated along the dominant dimension, depending on the heterogeneity characteristic of the lot. It is therefore utmost important to characterize the heterogeneity of the material, in order to detect to which degree non-random heterogeneity fluctuations are present along elongated or moving

lots, that is, the heterogeneity *between* extracted increments. Besides correct design of the sampling equipment for extracting the increments, as extensively reviewed in Section 4.1, one of three available sampling *modes* must be selected: systematic, stratified random or random. Choice of the optimal sampling scheme must be based on an initial heterogeneity characterization of the 1-dimensional lot. Variograms are used to characterize possible autocorrelation (1-dimensional heterogeneity) as a function of the distance between the extracted increments, which also allows identification of trends and periodic cycles (see Appendix A.2).

A.1. Heterogeneity of 1-dimensional lots

The extraction of correct increments from 1-dimensional lost must be delineated so as to make up "discrete, complete planar-parallel cut across the entire stream of material [. . .] chronologically ordered" [22]. The heterogeneity contribution, h_q, of each such increment, U_q, is defined as follows:

$$h_q = \frac{(a_q - a_L)}{a_L}\frac{M_q}{\overline{M}_q} = N_U\frac{(a_q - a_L)}{a_L}\frac{M_q}{M_L}$$

where M_q is the unit mass, $\overline{M}_q$ the average unit mass, a_q is the grade of the unit, N_U the number of units in the lot and a_L is the true concentration of the lot. The heterogeneity contribution h_q from a 1-dimensional increment is composed of three parts [8,11,12]:

1. A random, discontinues, short-range fluctuation component, reflecting the heterogeneity within the extracted increment, which is equal to the sum of all 0-dimensional sampling errors and the Total Analytical Error (TAE).
2. A non-random, continuous, long-range fluctuation term, reflecting longer-term *trends* in the process/lot over certain time/distance.
3. A non-random, continuous, cyclic term, reflecting *periodic* or *cyclic* behaviour of the process/lot.

In order to characterize the heterogeneity of a 1-dimensional lot the chronological order of the units must be included. For this characterization the so-called variogram is used.

A.2. Variogram

The variogram is a useful tool to highlight process variations (or stationary 1-dimensional heterogeneity fluctuations) and to characterize auto-correlation between sampled units with different spacings. A variogram is a plot of the average squared difference of a certain characteristic, such as the values of h_q between pairs of units, which are described as a function of distance or time [11]. A variographic analysis requires a complete set of representative increments, equidistantly extracted over a sufficiently long interval [22]. By quantifying autocorrelation as a function of distance or time between the sampling points – termed *lags* (j), the variogram provides valuable information in the form of the '*nugget effect*', the '*sill*' and the '*range*'. The relative and dimensionless lag parameter j describes the distance between two extracted units and is defined as:

$$j = \frac{\theta}{\theta_{\min}}$$

where θ is the sample distance and θ_{min} the smallest sampling interval. θ can be measured in various units like minutes, hours, product number, meters, etc., depending on the given situation. 50–60 increments are considered minimum for a variographic analysis [8,11,21]. If N_U increments are extracted, $N_U - 1$ pairs of units with distance θ, $N_U - 2$ pairs of units with distance 2θ, etc. are available. In practice, it is not necessary to calculated pairs for lags higher than half of measured series, $(1/2)N_U$ for the different pairs of units. The variographic function $V(j)$ is defined as 1/2 times the average of the squared difference in heterogeneity between the pairs of increment as a function of j:

$$V(j) = \frac{1}{2(N_U - j)}\sum_{q=1}^{N_U - j}(h_{q+j} - h_q)^2$$

Plotted variograms can have different appearances, however normally only three primary types of variograms are encountered: the increasing variogram (top-left), the flat variogram (top-right) and the cyclic variogram (bottom), here superposed on an increasing variogram.

As shown in Fig. A.1 (bottom) a variogram can easily reveal cyclic behaviour or periodicity. The sampling mode (systematic, random and stratified random) must under no circumstances being similar to these periodic/cyclic phenomena. For details about these different sampling modes the reader is referred to Gy [8], Pitard [23], Petersen and Esbensen [10], Halstensen [33], and Esbensen et al. [26]; the latter contains a collection of easily understandable examples of variograms of different process types, complete with examples of how to use the variogram for selection between appropriate sampling alternatives.

Interpretation of variograms is the most important step in variographic analysis, allowing to reveal trends in the variation, assessing of periodicity of cycles and the determination of the optimal sampling frequency. Three main features of the variogram are decisive, as depicted in Fig. A.2: the '*nugget effect*', the '*sill*' and the '*range*'.

The sill represents the average overall variance between the units, representing the maximum variation within a time series. It is therefore an indicator for spatial randomness. Once the variogram converges towards the sill, points in the time series are no longer correlated.

The distance (j) in which the variogram function is below the sill is called range, the between-increment distance below which the process exhibits auto-correlation. The degree of $V(j)$ reduction for decreasing lag is in direct proportion to the magnitude of spatial correlation between the sampled units.

The nugget effect is an indication for the *Minimum Practical Error* (MPE), estimated by extrapolating the variogram to $V(0)$. A time lag of 0 corresponds to that two identical units would have been extracted from exactly the same volume. This is a physical impossibility of course. Even though variograms are thus not defined for $j = 0$, auxiliary functions actually allows to extrapolate the variogram to $j = 0$ which results in valuable information – called MPE about the expected "zero-point variation" [22]. The MPE represents the expected level of all incorrect and correct sampling errors, as well as the Total Analytical Error (all 0-dimensional errors), of the sampling process applied, and is therefore considered of prime interest. Examples of complete variographic analyses can be found in [22].

A.3. Seven sampling unit operations (SUOs)

TOS can be summarized as a set of seven Sampling Unit Operations, representing a toolbox of principles and operations for correct sampling [12,22]. The first three SUOs constitutes principles that are normally applied *prior* to designing a new sampling procedure, where as SUO 4–7 mainly refer to practical sampling operations, but all SUOs find application wherever needed in order to comply with TOS:

SUO 1: Heterogeneity characterization of new materials, meaning a characterization of the 0-dimensional sampling variation by replication experiment (see Appendix A.4).
SUO 2: Characterization of 1-dimensional heterogeneity using variographic analysis (see Appendix A.2).
SUO 3: Transformation of 2- and 3-dimensional lots into 1-dimensional sampling situation whenever possible (see Section 2.3).
SUO 4: Application of composite sampling.
SUO 5: 'Homogenization' of lot or sample by mixing and/or blending.
SUO 6: Particle size reduction.
SUO 7: Representative mass reduction. Representative sampling can be defined as: representative primary sampling + representative mass reduction.

It is important to make clear that once a sample has reached analytical laboratory, no possibility exits to determine if the sample is representative of the lot it was extracted from. Therefore, representative sampling has to be ensured at all stages of the sampling process with the SUOs supporting a correct sampling process at all stages and at all scales.

A.4. Replication experiment

The *distributional heterogeneity* (DH) describes TOS all aspects of heterogeneity dependent upon the *spatial distribution* in the lot, in contrast to the *constitutional heterogeneity* (CH), which is dependent on the physical or chemical differences between individual lot units (grains, fragments, kernels, etc.). DH occurs due to stratification, segregation and/or local groups-of-fragments concentrations with a significant lower, or higher, analyte concentration than the average lot concentration. Only mixing or blending can actively reduce DH.

The quantitative effect of DH of a particular sampling process (including sample mass, sampling procedure, etc.) can be quantified by extracting a number of *replicate samples* and calculating the resulting empirical variance of the analytical results. This procedure, termed *replication experiment*, preferentially requires 10 replicated primary samples [34]. It is decisive that primary sampling and all subsequent sampling and mass reduction steps are free of any incorrect sampling errors (i.e. that only correct sampling errors are present) and are replicated in an identical way.

The standard deviation (STD) in relation to the average (X_{avr}) can be effectively expressed as a percentage, i.e. as the relative coefficient of variation (CV_{rel}):

$$CV_{rel} = \frac{\mathrm{STD}}{X_{avr}} \times 100$$

CV_{rel} represents the Global Estimation Error (GEE), the sum of all sampling errors (TSE) and the Total Analytical Errors (TAE). Therefore the CV_{rel} allows to compare numerical percentages resulting from f.ex. alternative sampling procedures.

Currently an extensive international effort is made to create a "horizontal sampling standard", designated to be "matrix-independent". This standard also focuses on developing specifications for a threshold/maximum percentage of CV_{rel} as a practical maximum acceptable sampling variance. A CV_{rel} corresponding to 20–35% has been suggested to be reasonable [34], carefully noting however that this threshold should not be applied for all systems but rather that this is a default threshold for all uncharacterized systems. CV_{rel} of less heterogeneous systems for example should be set to a level as low as 15–20% [23], while for *uniform systems* it must be as low as 5% (2%).

The issue is actually not as much the absolute level of this sampling quality index – the salient issue is that it must become mandatory to supply a relevant CV_{rel} for any sampling process, sampling equipment, etc. in order that the users of the ensuing analytical characterizations can make an *informed evaluation* of the complete sampling analysis result. We here call for such CV_{rel} characterization within the realm covered by biofuel standards and related fields.

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